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Summary

Selected recent developments associated with the use of glass for lasers are reviewed. These include new glass forming systems, the effects of glass composition on laser parameters, possibilities for additional lasing ions and transitions, nonlinear optical properties and laser-induced damage of glass, recent results in glass fiber lasers, and advances in glass laser operating techniques.

Introduction

In the 25 years since the first report of stimulated emission from neodymium in glass,[1] a large number of glasses have been explored for possible laser action. The number of actual demonstrated glass lasers, however, is very much smaller;[2] the number of commercially available laser glasses is smaller still.[3,4] The past decade has witnessed the discovery of many new glasses based on compounds not previously considered as glass progenitors. Most of the developments have been in the area of nonoxide glasses and of mixed anion glasses, however the range of oxide glasses has also continued to grow (see, for example, Ref. 5). These developments have greatly expanded the range of physical properties and laser parameters available to the glass laser designer.

The properties to be satisfied by a laser glass are many and varied. They include, for the host glass, the range of transparency, linear and nonlinear refractive indices, thermal-optic properties, thermal shock

resistance, and damage threshold and, for the lasing ion, the absorption spectrum, radiative and nonradiative transition probabilities, fluorescence wavelength, stimulated emission cross section, and spectroscopic inhomogeneities. Several of these properties and their variations with the chemical composition of the glass have been discussed previously.[6-10].
Which glass is best for a specific application depends on the requirements for the laser wavelength and pulse duration, the spectrum and duration of the pump source, small- or large-signal gain operation, and the optical configuration. The size of the glass components and their environment impose questions of production and chemical durability. Although a glass may have the best laser characteristics, cost and availability may be the final arbiters in the selection process.

Below we survey recent developments in selected areas of glasses and glass lasers which updates an earlier report presented at the Second Otto Schott Colloquium.[11] Again it is not possible to survey all physical properties of interest for glass lasers with any degree of thoroughness, therefore we concentrate principally on spectroscopic properties which are of fundamental importance for laser action.

Although we will be concerned exclusively with glass properties, significant improvements in glass lasers occur not only from glass developments but also from advances in operating techniques and better engineering. For example, heating and associated optical distortions in laser glass arising from broadband optical pumping can be greatly reduced by exciting directly into the upper laser level using semiconductor laser diodes. Improved laser diode technology has led to the recent demonstration of a diode-pumped monolithic CW Nd:glass laser.[12] In large, high-average-power laser systems, various cooling schemes and optical

configurations have been proposed to reduce distortions and increase overall performance limits.[13] Developments such as these can have an equal or greater impact than those arising from improvements in glass properties.

Glass Compositions

The number of new glass forming systems discovered in recent years is large and still growing and includes both oxide and nonoxide glasses. We will not attempt to review this rapidly proliferating field in detail here. Instead, examples of several nonoxide glasses - some new and some old - are listed in Table I.[14-21] The extent of the glass forming regions for these multicomponent glasses vary widely; a representative composition of each is given but the reference cited should be consulted for information about the range of compositions and physical properties possible. One thrust of the compositional studies has been to extend the infrared transparency to longer wavelengths by introducing heavy metal ions. As can be seen from Table I, halide glasses have been a subject of major activity.[30,31]

In addition to multicomponent glasses containing a single anion species, glasses containing a mixture of anions exist. For example, glasses can be formed with compositions ranging from phosphates with only a few mole percent fluoride to mixed fluoride glasses with only a few mole percent phosphate. Several mixed anion glasses are given in Table II.[32-40] Because the anions are the lasing ion ligands, they have a large effect in determining the spectroscopic properties. Mixed anion nearest-neighbor coordination is also possible. This introduces an additional degree of local disorder into an already disordered structure and increases the inhomogeneity of the spectroscopic properties on the lasing ion.[41] This appears as inhomogeneous line broadening in absorption and fluorescence spectra and as site-dependent

cross sections and radiation and nonradiative decay rates. The probability of having mixed anion coordination has been discussed in terms of the theory of hard and soft acids and bases.[42]

It is evident from the glass compositions in Tables I and II and the many known oxide glass forming systems[43] that, depending on the chemical composition of the host glass , the local fields at a laser ion site can vary greatly. All glass lasers to date have a rare earth as the active ion.[2,4] The glasses included in the above tables are, in many cases, those in which rare earths have been added to investigate how changes in local field affect spectroscopic properties and laser parameters. Spectroscopic data obtained from small ($\sim$1 cm^3) samples combined with simplified computer models have been used to estimate relative laser performance in both the small-signal[44,45] and large-signal[46] or saturated gain regimes. Therefore many different glasses can be surveyed and predictions made about the effects of compositional changes without actually demonstrating laser action.

Stimulated Emission Cross Sections

One of the most important parameters for laser action is the stimulated emission cross section. It determines the gain and the rate of energy extraction. The stimulated emission cross section for a trivalent rare earth transitions is given by

$$\sigma = \frac{8\pi^3 e^2}{3hc(2J + 1)} \frac{(n^2 + 2)^2}{n} \frac{\lambda_p}{\Delta\lambda_{eff}} S(J,J'), \tag{1}$$

where n is the refractive index of the host, λ_p is the wavelength of the emission peak, S is the line strength of the transition, and $\Delta\lambda_{eff}$ is the effective linewidth of the emission between states J and J'. Since the emission bands of rare earths in glass are usually asymmetric and consist of inhomogeneously broadened transitions between several Stark levels, an

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effective linewidth obtained by integrating over the band and dividing by the peak intensity is used in Eq. (1).[47]

Of the quantities determining σ in Eq. (1), S, $\Delta\lambda_{eff}$, and n are strongly host glass dependent. The variation of S is governed by the Judd-Ofelt intensity parameters; examples of their variation with glass composition have been given earlier.[11] The rare-earth ligands have the greatest influence on the linewidth. In general, the smaller the anionic field strength, the smaller the Stark splitting and the narrower the effective linewidth. Therefore $\Delta\lambda_{eff}$ is narrowed by using monovalent halide rather than divalent oxide anions. Among different glass-forming systems, the narrowest linewidths appear when the rare earth can establish the most symmetric, chemically uniform coordination sphere possible. This occurs when the rare earth does not have to compete with the glass-forming cations for the available ligands. Finally, for a given glass network former, $\Delta\lambda_{eff}$ generally increase with increasing charge and decreasing size of the modifying cations.[48] These rules and the increase of σ with n[49] have been used to tailor stimulated emission cross sections.[42]

Neodymium lasers are by far the most studied glass lasers. Because of the associated large database, we restrict the comparisons of spectroscopic properties to those of Nd^{3+}. Many of the conclusions and trends, however, are also applicable to other laser ions. The ranges of effective stimulated emission cross sections for the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition of Nd^{3+} observed for different glass types are summarized in Table III. Since all compositional variations have not been investigated, the values cited are not necessarily the extreme values possible. For silicate glasses , σ varies by a factor of about four by changing the host composition from a simple alkali silicate to a high-refractive-index bismuth silicate. The peak cross sections

obtainable for phosphates are larger than for silicates. This is not because
the line strengths are significantly larger but because the effective
linewidths are narrower. Some tellurite glasses have even larger cross
sections than for phosphates, not because S or $\Delta\lambda_{eff}$ are more favorable
but because of the large refractive index of the host glass.[49]

Rare earths in halide glasses have been the subject of several recent
studies.[56,57] As expected, the Nd^{3+} emission from halide glasses has
narrower linewidths than the narrowest linewidths for oxide glasses
(phosphates).[11] For fluoroberyllate glasses , this does not result in
larger cross sections because the line strengths are smaller than for
phosphate glasses. Chloride glasses combine a small $\Delta\lambda_{eff}$ with a large
line strength and a high refractive index to yield stimulated emission cross
sections larger than those for any oxide glass.[42] The high index, narrow
linewidth, covalently bonded chalcogenide glasses have the largest Nd^{3+}
cross sections observed thus far. Overall, about an order of magnitude change
in Nd^{3+} cross section is possible by varying the host glass composition.

The final column in Table III lists the ranges of cross sections for some
current commercial Nd laser glasses. The number of glass types and the range
of parameters available are very restricted. These glass compositions were of
course selected to have of combination of good physical properties and melting
characteristics as well as good optical and laser properties. The message
remains, however, that a much larger compositional space exists for laser
glass exploitation.

The behavior of the stimulated emission cross section and spectroscopic
properties of other rare-earth ions is expected to be similar, although not
identical, to that exhibited by Nd^{3+}. Few comparable compositional studies
exist for other lanthanide ions. Recently the stimulated emission cross

section for $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition of Yb^{3+} was determined from

absorption and emission measurements of 4. different oxide, fluoride, and

oxyfluoride glasses .[58] The effective peak cross sections at 293 K ranged

from approximately 0.3 to 0.8 pm^2. The largest values occur in borate and

phosphate glasses; the smallest values occur in silicate and

low-refractive-index fluoride glasses. The results show again how systematic

variations in cross sections with changes in modifier ions can be used to

tailor stimulated emission cross sections and fluorescence lifetimes.

Laser Ions

As noted earlier, glass lasers have used trivalent rare earths

exclusively as the active ion.[2] The number of different rare earths and

transitions lased in glasses is, however, much smaller than that in crystals.

Crystalline lasers have also utilized ions from other transition metal

groups.[59] In the last few years, motivated in part by the desire for

tunable solid-state lasers, an increasingly large number of potential laser

ions have been investigated.[60] These have included:

   i)   5d-4f transitions of Ce^{3+}(LiYF$_4$) and other rare-earth ions,

   ii) $^4T_2$-$^4A_2$ transitions of Cr^{3+} in low-crystal-field sites (BeAl$_2$O$_4$, garnets),

   iii) ^2E-$^2T_2$ transitions of Ti^{3+} (Al$_2$O$_3$),

   iv) various fluorescence transitions of 4d and 5d group ions, e.g., Rh^{2+} (RbCaF$_3$),

   v) $3d^{10}$-$3d^9 4s$ transitions of Cu^+,

   vi) charge transfer transitions of Ti^{4+} (Li$_4$Ge$_5$O$_{12}$).

(The compounds in parentheses are crystals from which laser action has been reported.) This list plus previously studied ions by no means exhausts the known types of luminescent species in solids, hence future additions are anticipated.

Investigations and demonstrations of new lasing schemes in glasses have not been as extensive in glasses as in crystals. One reason is that the vibrational modes in glass extend to higher frequencies than in most crystals. This leads to a greater probability for nonradiative relaxation by multiphonon emission and, as a result, a smaller number of efficient fluorescing states. In the case of trivalent rare earths, relaxation rates can be reduced by using heavy metal fluoride glasses as hosts because of their lower vibrational frequencies.[57] Another problem plaguing glass studies arises from the inherently inhomogeneous spectroscopic properties. To obtain detailed information about the distributions of energy levels and transition probabilities, one must resort to site selection spectroscopy using laser-excited fluorescence techniques.[6,62]

Studies relevant to some of the lasing schemes listed above have been conducted. Trivalent cerium, for example, has been added to beryllium fluoride glasses and exhibits fluorescence bands and lifetimes comparable to those from Ce-doped fluoride crystals that have lased.[63] In the case of Cr^{3+}, nonradiative rather than radiative processes have been found to be the dominant cause of relaxation in a wide variety of oxide and fluoride glasses,[64] thus making glasses less attractive than crystals as host materials.[65] Short lifetimes for the $^4 _2$ excited state of Cr^{3+} are not, however, necessarily detrimental if a fast pump source is available to create an inverted population and a stimulated emission rate greater than the spontaneous decay rate can be achieved. Fluorescence studies of Ti^{3+} in

fluorophosphate glass were reported recently but no attempt to obtain lasing was made.[66] Although the 3d transition group ions have been explored extensively for solid-state laser possibilities, the spectroscopy of the 4d and 5d transition groups has been less thorough. They have, however, been the subject of a recent investigation.[67] In addition, gain was reported for a Rh^{2+}-doped $RbCaF_3$ crystal.[68] I am unaware of comparable studies of these ion groups in glasses. The spectroscopic properties of monovalent copper in glass have been studied[69] and some evidence of gain has been observed in a Cu^+-doped aluminoborosilicate glass.[70] The gain was very small, but there are no similar reports for Cu^+ lasing in crystals. This laser requires an ultraviolet pump source, thus color centers may be generated which introduce losses. Gain in the blue green spectral regions associated with the broadband emission of Ti^{4+} has thus far only been reported for a lithium germanate crystal.[71]

The above examples reveal that there are numerous lasing possibilities in glasses involving ions and transitions that are relatively unexplored. Because of the dependence of spectroscopic properties on glass compositions and the rich glass compositional space available, systematic studies of glass lasing schemes should yield new results of potential scientific and technological interest. The field of lasers, however, has reached a level of maturity where the discovery of just another laser is frequently not significant. Identifying specific laser features not readily available from other system may establish whether the efforts necessary to demonstrate lasing are warranted.

High-Power Lasers

In high-power glass lasers,[72] the light intensity may become so large

that it induces changes in the optical properties of the laser glass and other transmitting optical components. The intensity-dependent optical properties are characterized by the nonlinear refractive index coefficient n_2 and the two-photon absorption coefficient β which have been described previously.[11] (Tabulations of n_2 and β values for glasses are published.[73,74]) Effects of self-focusing and nonlinear absorption are minimized by using low-n_2 glasses.[75] Although accurate calculations of n_2 are not possible, empirical relationships for n_2 in terms of the refractive index n and the Abbe number ν have been derived from measured values of n_2 for a large number of different oxide and halide glasses.[76] Large reductions in n_2 are possible by using low-index, low-dispersion glasses of which beryllium fluoride glasses are particularly attractive.[77]

Estimates of n_2 values are valid in the long wavelength limit, that is, for wavelengths far removed from the fundamental absorption edge. The dispersion of n_2 as the wavelength approaches an absorption band has not been measured. Such measurement are needed to guide the theoretical treatment and quantitative prediction of these effects.

Intensity-dependent losses in glass due to multiphoton absorption can be avoided by using wide band gap materials. These are usually also low-index glasses and beryllium fluoride glasses are again attractive.[78] Two-photon-induced solarization is another intensity-dependent phenomena that has been detected in borosilicate glasses using sensitive photothermal lensing techniques.[79] A one-photon bleaching process was also active and limited the amount of solarization. These affects in glasses are further complicated by the possible existence of a distribution of color center generation and annihilation rates.

The rate of energy extraction from a laser is ultimately limited by the

maximum intensity per unit area that can be propagated without catastrophic damage to the glass. Damage may occur either in the bulk, due for example to metallic particles and other absorbing imperfections,[80] or at the surface due to associated physical or chemical defects.[81] The dominant source of damage is frequently dependent on the manufacturing and fabrication processes. For high-quality optical glasses, the threshold for surface damage is generally lower than that of the bulk.

Metallic platinum inclusions have a long history as the cause of damage in laser glass. In recent years, they have limited the performance of Nd-doped phosphate and fluorophosphate glasses developed for large laser systems used in inertial confinement fusion experiments. These particles range in size from less than 5 to about 100 µm and are introduced from the crucible during the glass melting process. When irradiated by an intense laser beam, the front surface of the inclusion is vaporized. This causes a shock wave that is propagated through and fractures the glass. Thermal modeling of this process has been carried out, but not sufficiently to predict crack growth.[82]

The formation of metallic platinum inclusions is affected by the oxygen content of the process gas, the melt temperature and temperature uniformity, the processing time, and the platinum solubility in the glass. By increasing the oxygen content of the processing gas and using other proprietary additives, dissolution of platinum particles in phosphate glass melts has been increased and the number of inclusions dramatically reduced.[82]

Laser-induced damage also occurs at coatings applied to optical elements to reduce reflective losses. Porous silica surface layers have been found to have higher resistance to damage than traditional vacuum-deposited antireflection coatings. Recently a porous silica coating prepared from a

silica sol in ethanol was applied to optical glass and nonlinear optical materials and increased the damage threshold significantly.[83]

Fiber Lasers

At the other extreme from large, high-power lasers are small fiber laser oscillators and amplifiers of interest for integrated optics and telecommunications applications. Lasing of Nd-doped glass fibers was demonstrated in the 1960s. Whereas these were multimode devices, low-threshold, single-mode Nd fiber lasers have recently been reported based on low-loss silica fibers produced by a extended MCVD fabrication process.[84] Rare-earth dopant concentrations of about one part per thousand have been achieved while maintaining low losses; construction of 300-m long amplifiers and lasers has also been demonstrated.[85] Using a GaAlAs laser diode as a pumping source, CW lasing of Nd^{3+} at 1088-nm was obtained at room temperature with a laser threshold of less than 1 mW. Using an Ar-ion laser pump, a tuning range of 80-nm (the largest reported thus far) is possible. Laser action has also been observed for silica fibers doped with Er^{3+} (1.55 μm) and Pr^{3+} (1.1 μm).[86]

The extremely large inhomogeneous linewidths fluorescence for rare earth transitions in fused silica reflects the large distribution of physically different sites that are possible in this material. Recently, it was found that when $Nd:SiO_2$ glass is co-doped with Al or P in concentrations about 10 times that of Nd, dramatic changes are observed in the width and intensity of the fluorescence spectrum.[87] This is attributed to the formation of a co-dopant solvation shell around the Nd^{3+} ions. Such techniques provide an additional means of varying the local environment and thereby altering spectroscopic properties and laser parameters.

Fluoride glasses, both beryllium fluoride and heavy metal fluoride, should have smaller intrinsic scattering losses than silica in the near-infrared. Thus far these ultralow losses have not been achieved because of larger losses due to absorbing impurities and extrinsic scattering. Surveys of the optical absorption by 3d transition metals and rare earths in zirconium fluoride glasses[88] and by rare earths in beryllium fluoride glasses[89] indicate that, depending upon the operating wavelength, the concentrations of these impurities will have to be reduced to the level of parts per billion to realize the predicted low-loss fiber performance.

Acknowledgment

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Table I. Examples of nonoxide glasses.

Glass type	Representative composition (mol%)	Reference
Fluorides		
Beryllium fluoride	$60BeF_2-20KF-10CaF_2-10AlF_3$	14
Cadmium fluoride	$30CdF_2-40BaF_2-30ZnF_2$	15
Lead fluoride	$50PbF_2-25MnF_2-25GaF_3$	16
Aluminum fluoride	$45AlF_3-35CaF_2-20BaF_2$	17
Zirconium fluoride	$62ZrF_4-33BaF_2-5LaF_3$	18
Hafnium fluoride	$62HfF_4-28BaF_2-10LaF_3$	19
Thorium fluoride	$40ThF_4-20BaF_2-39YbF_3$	20
Scandium fluoride	$50ScF_3-20YF_3-40BaF_2$	21
Zinc fluoride	$40ZnF_2-30YF_3-30BaF_2$	22
Manganese fluoride	$50MnF_2-30DyF_3-20BaF_2$	23
Heavy metals fluoride	$28ThF_4-28YbF_3-15BaF_2-28ZnF_2$	24
Chlorides		
Bismuth chloride	$60BiCl_3-40KCl$	25
Thorium chloride	$40ThCl_4-30NaCl-30KCl$	26
Bromide		
Bismuth bromide	$70BiBr_3-20TlCl-10PbCl_2$	27
Sulfides		
Aluminum sulfide	$75Al_2S_3-25La_2S_3$	28
Gallium sulfide	$70Ga_2S_3-30La_2S_3$	29

Table II. Examples of mixed anion glasses

Glass type	Representative composition (mol%)	Reference
Mixed Halides		
Chloride-iodide	$50ZnCl-50KI$	32
Bromide-chloride	$60BiBr_3-25TlCl-15PbCl_2$	27
Oxyhalides		
Phosphate-fluoride	$5Al(PO_3)_3-12M^IF-51M^{II}F_2-32AlF_3$	33
Phosphate-chloride	$35P_2O_5-35Na_2O-30ZnCl_2$	34
Zirconia-fluoride	$40ZrO_2-20LiPF_6-40KPF_6$	35
Tellurite-chloride	$66TeO_2-11BaO-23ZnCl_2$	36
Sulfate-chloride	$40Na_2SO_4-60ZnCl_2$	32
Oxysulfides		
Silicate-sulfide	$75SiO_2-25Na_2S$	37
Gallium-lanthanum	$70Ga_2S_3-30La_2O_2S$	38
Oxycarbide	$57SiO_2-25Al_2O_3-15MgO-3SiC$	39
Oxynitride	$Y_2O_3-AlN-SiO_2$	40

Table III. Stimulated emission cross sections for the $^4F_{3/2} \to {}^4I_{11/2}$ transition of Nd^{3+} in different glasses at 295 K. Cross sections for commercial laser glasses are from Refs. 3 and 4.

Glass	n_d	Cross section $\sigma(pm^2)$	Ref.	Commercial glasses-$\sigma(pm^2)$
Oxides				
Silicate	1.46-1.75	0.9-3.0	50, 51	1.5-2.9
Germanage	1.61-1.71	1.7-2.	51	
Tellurite	2.0 - 2.1	3.0-5.	49, 51	
Phosphate	1.49-1.63	2.0-4.	51, 52, 53	3.0-4.5
Borate	1.51-1.69	2.1-3.	51	
Halides				
Fluoroberyllate	1.28-1.38	1.6-4.0	51, 54	
Fluorozirconate	1.52-1.56	2.9-3.0	18	
Fluorohafnate	1.51	2.6	51	
Fluoroaluminate	1.41-1.48	2.2-2.7	51	
Chloride	1.67-2.06	6.0-6.5	42	
Oxyhalides				
Fluorophosphate	1.41-1.56	2.2-4 3	51	2.5-5.7
Chlorophosphate	1.51-1.55	5.2-5 4	55	
Chalcogenides				
Sulfide	2.1 - 2.5	6.9-8.2	28, 38	
Oxysulfide	2.4	4.2	38	